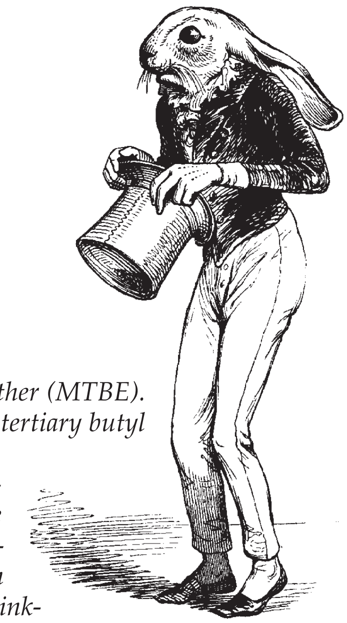
MTBE

# Tertiary Butyl Alcohol (TBA)

# MTBE May Not Be the Only Gasoline Oxygenate You Should Be Worrying About



*By Steven C. Linder*

*Over the past several years, the spotlight has been on the gasoline additive methyl tertiary butyl ether (MTBE). However, MTBE may not be the only additive of concern at many gasoline releases. There is also tertiary butyl alcohol (TBA)—one of the more significant gasoline oxygenate additives other than MTBE.*

*I first learned heard about TBA in August 1998 at a meeting about pilot-testing drinking water treatment technologies at the City of Santa Monica's Charnock Wellfield. Many of us were taken by surprise when the consultant to the potential responsible parties (PRPs) associated with the city's MTBE contamination problem brought up the subject of TBA. He explained that TBA, as well as MTBE, had been detected in the monitoring wells surrounding the drinking water wells and that TBA was likely to be present in the drinking water wells when pumped.*

*At the time, the PRPs were in a temporary settlement with the City of Santa Monica and Southern California Water Company requiring that they pay more than $4 million per year for purchased imported replacement drinking water. Contending that wellhead treatment was much less costly than replacement water, the PRP companies had, in my opinion, a tremendous incentive to get wellhead treatment on line as soon as possible.*

*At the meeting, we went on to discuss how TBA could likely have a significant influence on the treatment technologies used to clean up petroleum releases, because air stripping and granular activated carbon were not thought (based on theoretical evaluation) to be effective technologies for TBA. Because TBA had been detected in the wells and identified as an issue, the treatment cost estimates increased substantially.*

## What Is TBA?

TBA (CAS# 75-65-0) is a colorless solid or liquid (above 77°F) with a camphor-like odor. One study reports that the odor threshold for TBA is at a vapor concentration of approximately 609 ppm. The chemical formula for TBA is $(CH_3)_3COH$. TBA has a research octane rating of 103, a molecular weight of 74.1, and a specific gravity of 0.79. It is miscible in water. It has a Henry's law constant of 121E-5 (atm-m$^3$)/(g-mole), which means it's even harder to air strip than MTBE. It has a log $K_{oc}$ of 1.57, which means it doesn't adsorb readily to carbon. And, it has a log $K_{ow}$ of 0.35, which means it prefers to stay in water, once it is there.

TBA has many uses—in extraction of drugs, as a denaturant in ethanol, as a dehydration agent in the manufacture of flotation agents, in fruit essences, in plastics, in perfumes (as a solvent), as a chemical intermediate, and as an additive/blending agent in unleaded gasoline.

## Why Is TBA in Gasoline?

TBA is used as a gasoline additive/blending agent. Oxygenates, particularly alcohols, have a long history of use in motor fuels—going back to the beginning of the twentieth century, when ethanol was first promoted for blending into gasoline. At various times, different alcohols (e.g., methanol, isopropyl alcohol, and TBA) were of commercial interest in gasoline blending because of their special performance properties. TBA has been added to gasoline as an antiknock compound.

The Atlantic-Richfield Company (ARCO) began using gasoline-grade tertiary-butyl alcohol (GTBA) in 1969 to improve octane. In 1979, ARCO received approval from EPA to use GTBA at up to 7.0 percent by volume in unleaded gasoline. Also in 1979, Sun Oil Company received an EPA waiver that allowed the use of 2.75 percent by volume methanol along with 2.75 percent by volume GTBA in a blend with unleaded gasoline. ARCO Petroleum Products received a waiver in 1981 and introduced an oxygenate blend containing about 9.5 percent by volume of an equal mixture of methanol and GTBA in Pennsylvania. EPA also has granted waivers for blends of gasoline and GTBA up to 3.5 mass percent oxygen content (16 vol % TBA) and for various blends of methanol and GTBA or other higher-molecular-weight alcohol (cosolvents).

TBA is an impurity in commercial-grade MTBE, which commonly contains methanol and TBA as impurities. In some production processes, TBA is a precursor to MTBE. I am not aware of any publicly available studies that clearly identify the TBA impurity concentration ranges likely to be found in commercial-grade MTBE. (See Figure 1.)

## Does TBA Biodegrade Readily?

Unlike the linear alcohols methanol and ethanol, TBA is not easily degraded. Studies have shown no degradation of TBA in anerobic environments and some degradation in aerobic conditions. I understand that TBA was observed to degrade in a few weeks from water that had been collected from the Santa Monica Charnock Wellfield, spiked with TBA and stored in drums.

MTBE is a highly stable compound that is resistant to both biological and chemical reactions occurring

FIGURE 1

**Partial Diagram of MTBE and TBA Potential Environmental Transformations**

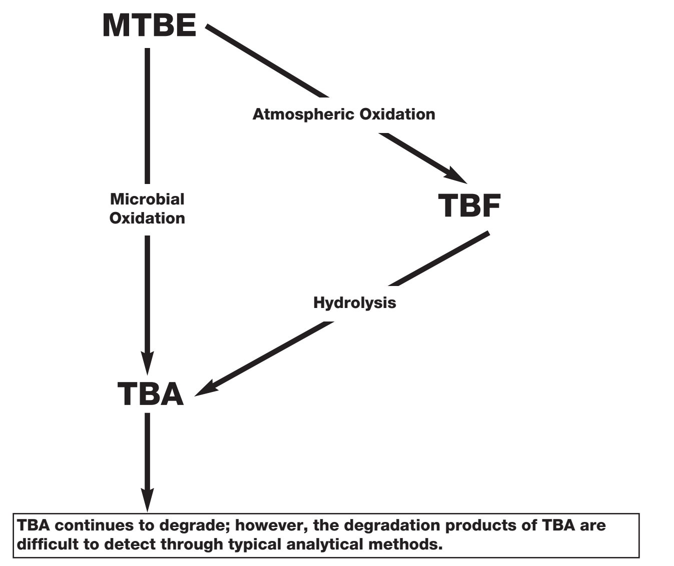
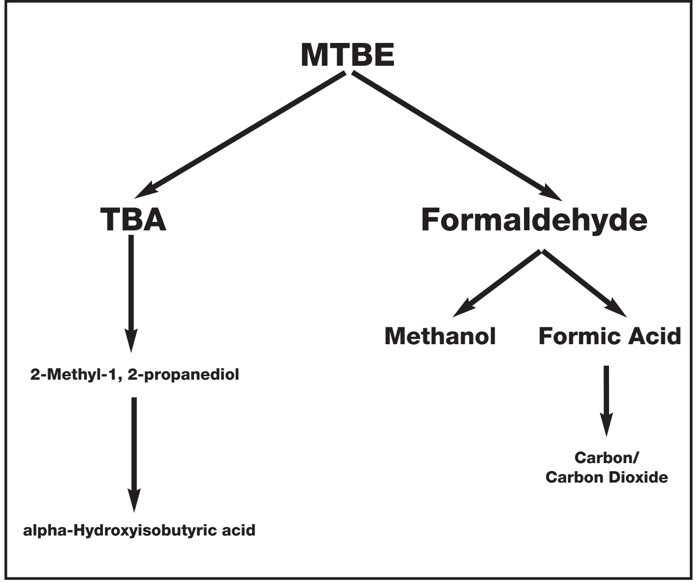



FIGURE 2

**Partial Diagram of MTBE and TBA Potential Metabolic Transformations**




in the environment. However, under some geochemical and microbial conditions within an aquifer, MTBE may degrade slowly. Some studies have shown accumulation of TBA after it has formed in association with the degradation of MTBE. In these circumstances, TBA may be found as a degradation product of MTBE.

## Has TBA Been Found at LUST Sites?

TBA can be a common contaminant in an environment where there have been releases of oxygenated fuels. For example, most of the service station sites examined as part of the Charnock (Santa Monica) MTBE investigation have detectable levels of TBA present in soil and/or groundwater. TBA has been detected at concentrations as great as 18,000 $\mu$g/L in groundwater near source areas of groundwater plumes that originate at the gasoline stations examined as part of the Charnock Wellfield investigation. TBA has also been detected in groundwater at gasoline releases in the South Lake Tahoe area.

## What Concentrations Are of Concern for TBA?

The California Department of Health Services has established a Drinking Water Action Level of 12$\mu$g/L for TBA. Drinking Water Action Levels are health-based advisory levels established by the Department of Health Services for chemicals for which primary maximum contaminant levels have not been adopted.

On September 12, 1997, New Jersey issued an Interim Specific Groundwater Criterion of 100 $\mu$g/L for TBA. New Jersey lowered the concentration that it recommends as a goal for groundwater cleanups and for guidance in situations where groundwater is contaminated with TBA from 500 $\mu$g/L to 100 $\mu$g/L based on the 1995 National Toxicology Program TBA drinking water study on rats and mice.

In May 1995, as part of the National Toxicology Program, the National Institutes of Health published a paper regarding toxicology and carcinogenesis of TBA in rats and mice. The study concluded the following:

> "Under the conditions of these 2-year drinking water studies, there was some evidence *of carcinogenic activity* of *t*-butyl alcohol in male F344/N rats based on increased incidences of renal tubule adenoma or carcinoma (combined). There was no evidence *of carcinogenic activity* in female F344/N rats receiving 2.5, 5, or 10 mg/mL *t*-butyl alcohol. There was equivocal evidence *of carcinogenic activity* of *t*-butyl alcohol in male B6C3F1 mice based on the marginally increased incidences of follicular cell adenoma or carcinoma (combined) of the thyroid gland. There was some evidence *of carcinogenic activity* of *t*-butyl alcohol in female B6C3F$_1$ mice based on increased incidences of follicular cell adenoma of the thyroid gland."

In addition, when ingested, MTBE initially metabolizes to yield TBA and formaldehyde. (See Figure 2.)

## What Analytical Methods Should Be Used for TBA Quantification?

TBA presents even greater analytical difficulties than those presented by MTBE. However, commercial laboratories have been able to achieve detection levels for TBA of 10 $\mu$g/kg in soil and 5 $\mu$g/L in water and quantification levels of 20 $\mu$g/kg in soil and 25 $\mu$g/L in water as required by EPA and State of California orders.

Extensive work by the USGS, Lawrence Livermore, and many other laboratories indicate that the ethers and TBA are measurable using purge-and-trap GC in conjunction with any of the determinative methods (8015, 8021, or 8260). Based on

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■ **TBA** *from page 19*

studies of the most widely used oxygenate, MTBE, potential analytical problems exist with methods 8015 or 8021. MTBE can be misidentified when other gasoline components are present, because of coelution of MTBE with these components. This misidentification is most pronounced with method 8015, which uses the nonselective FID detector, but it can be significant even if a PID detector is used. Similar misidentifications are likely when using methods 8015 or 8021 for any ether and/or TBA.

Clinton Church, Paul Tratnyek, and Jim Pankow, of the Oregon Graduate Institute, have developed a direct aqueous injection–GC/MS method for MTBE and its degradation products. They report that this method is able to achieve a detection limit of 0.1 $\mu$g/L for both MTBE and TBA.

As part of the Charnock MTBE treatability testing, data quality review procedures for TBA analyses by a mobile laboratory identified high-biased TBA results caused by tert-butyl formate [TBF (CAS# 762-75-4)] hydrolysis to TBA. Therefore, appropriate care (sample storage, preservation, and holding times) should be taken when handling samples to avoid high-biased TBA results.

## What Technology Can Be Used to Remove TBA from Water?

GAC isotherm and accelerated column tests performed by two major granular activated carbon (GAC) suppliers predicted that TBA will poorly adsorb to GAC when compared to MTBE adsorption. However, during pilot treatability testing at the City of Santa Monica's Charnock Wellfield, data appeared to show TBA removal by GAC.

During this testing, TBA was spiked to achieve a concentration of 200 $\mu$g/L. TBA was removed to below detection levels without any acclimation or transition period in a one-ton carbon vessel. However, in smaller GAC pilot columns, removal of TBA required a transitional period of approximately three weeks. Prior to the acclimation, TBA effluent results were consistent with the GAC isotherm and accelerated column tests. Data generated at a pump and GAC treatment facility adjacent to the City of Santa Monica's Arcadia Wellfield also show TBA removal through GAC vessels. Therefore, TBA is likely destroyed by biological activity in the GAC vessels.

Literature indicates that TBA is highly soluble in water and has a low Henry's law constant, which suggests that air stripping would not be significantly effective because of poor mass transfer of TBA from the aqueous phase to the vapor phase. From what I have been told, this theory appears to be true for a large treatment system that recently went into operation as part of the Santa Monica Charnock project.

At the Charnock Wellfield, UV-oxidation treatment was tested using Calgon's UV-peroxide technologies for water containing known spiked concentrations of MTBE and TBA. During the UV-oxidation tests, treatment of water spiked with MTBE at 1,000 ppb and TBA at 400 ppb required 40 percent more energy than treatment of water spiked with only 1,000 ppb MTBE. UV-oxidation treatment is a viable technology for treatment of water containing TBA. However, UV-oxidation technologies need to be carefully monitored and controlled to assure their effectiveness and avoid unwanted treatment by-products.

Synthetic resin sorbtion technologies have also been tested and found to show promise in aqueous-phase MTBE treatment. Some studies indicate that synthetic resins may be a more cost-effective sorption technology for TBA-contaminated water.

## Not to Be Ignored

TBA should not be ignored when addressing gasoline releases. It is a likely contaminant of concern at many LUST sites, although its concentrations are typically lower than those of MTBE at most sites. TBA is a very stable compound in the environment and may not readily degrade in groundwater in many aquifer settings.

From a toxicological point of view, exposure to TBA elicits both noncancer and systemic toxic responses, as well as evidence of carcinogenicity. Furthermore, formaldehyde is an in vivo metabolic product of TBA exposure, and EPA has determined that formaldehyde is a probable human carcinogen (class B1). TBA contamination can be more difficult than MTBE to quantify in water samples, and it is more difficult and costly to remove from water.

Clearly, further research and study is needed to better understand the significance of TBA related to gasoline releases. ■

*Steven Linder is an Environmental Engineer with EPA Region 9. He has been a project manager for the Charnock/Santa Monica MtBE Pollution project for the last three years. For more information, contact Steve at linder.steven@epa.gov or (415) 744-2036.*

# For More Information...

*...about TBA, check out the following Web sites:*

www.chevron.com/prodserv/bulletin/motorgas/sidebars/oxygenates.html

ntp-server.niehs.nih.gov/htdocs/LT-studies/tr436.html

www.dhs.ca.gov/ps/ddwem/chemicals/mcl/actionlevels_category1.htm

www.lyo.com/html/products/product-selector/tba/etbe-mtbe.htm

ntp-server.niehs.nih.gov/htdocs/Levels/Tr436levels.Html

www.healtheffects.org/Pubs/oxyprog.htm

www.epa.gov/region09/cross_pr/mtbe/charnock/

www.dhs.ca.gov/ps/ddwen/chemicals/mcl/actionlevels_category1.htm

www.ocwd.com/nwri/

www.epa.gov/swerust1/oxygenat/oxytable.htm

cgr.ese.ogi.edu/MTBE/